Mechanistic Modeling Framework
for Predicting Extreme Battery Response:
Coupled Hierarchical Models for Thermal, Mechanical, Electrical and (Electro)chemical Processes

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2015 DOE Vehicle Technologies Review
June 2015

Project # ES198

Overview

Timeline

- Project start: 9/22/13
- Project end: 1/10/15
- Percent complete: 65% spent, 75% duration

Budget

- Total project funding
  - DOE share: $1500K
  - No cost share
- Funded 9/21/13 for FY14-15: $1500K

Barriers

- Abuse tolerance and associated safety concerns is serious public acceptance issue.
- Lack of predictive battery design models with infrastructure for general chemistry and phase change modeling.

Partners

- Sandia National Laboratories (lead)
  - Electrochemical and thermal modeling
- Oak Ridge National Laboratory
  - CAEBAT open architecture integration
- Colorado School of Mines
  - Upscaling of pore-level models

Relevance/Objectives

- <u>Objectives</u>: : Facilitate advanced battery modeling with modeling framework based on fundamental material properties.
    - Deliver a software architecture solution that can lead to the development of predictive mechanisms.
    - Allow recent material developments to be easily incorporated.
        - In three issues of *J. Electrochem. Soc*. (vol. 161, Issues 6-8) there were more than half a dozen examples *each* of thermodynamic, transport and kinetic data or parameters. How do you implement new parameters monthly to keep up?
    - Demonstrate capabilities by addressing root causes and implications of thermal runaway of Li-ion batteries.
    - <u>Focus this period</u>: Addition of chemistry and physics models relevant to battery abuse scenarios including to 1D model
        - Energy equations,
        - Porous flow allowing gas generation,
        - Solid mechanics.
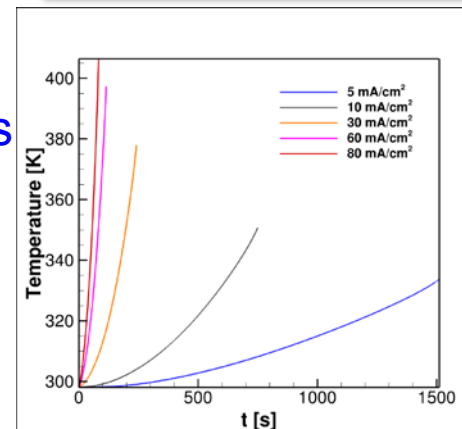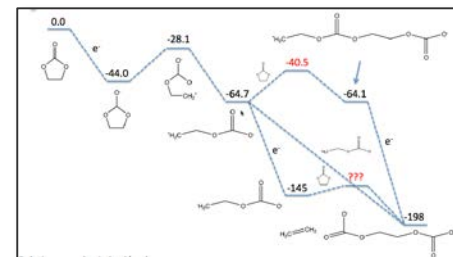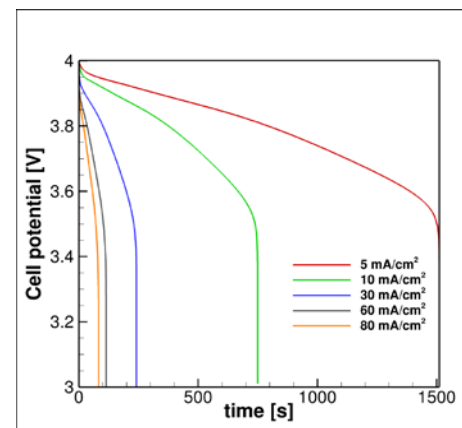
Key Objectives:

- Port 1DElectrode models (C++ Modular Object oriented) from Sandia's Thermal Battery program to the CAEBAT architecture.
- Develop consistent thermodynamic/transport models of the entire cell using CANTERA an open source constitutive modeling package
- Add partial saturation and solid mechanics models to CAEBAT to model gasification and stress-induced degradation phenomena
- Build SEI Models that can predict the autocatalytic temperature behavior experimentally observed
- Upscale microstructure calculations to the macrohomogeneous scale using both averaged results and statistical distributions.
- Develop new models for thermal runaway processes within Li-ion batteries that are based on consistent thermodynamics models.

- Develop a collaborative research program by publishing as open source, and invite other research groups to participate (http://github.com/cantrilbat)
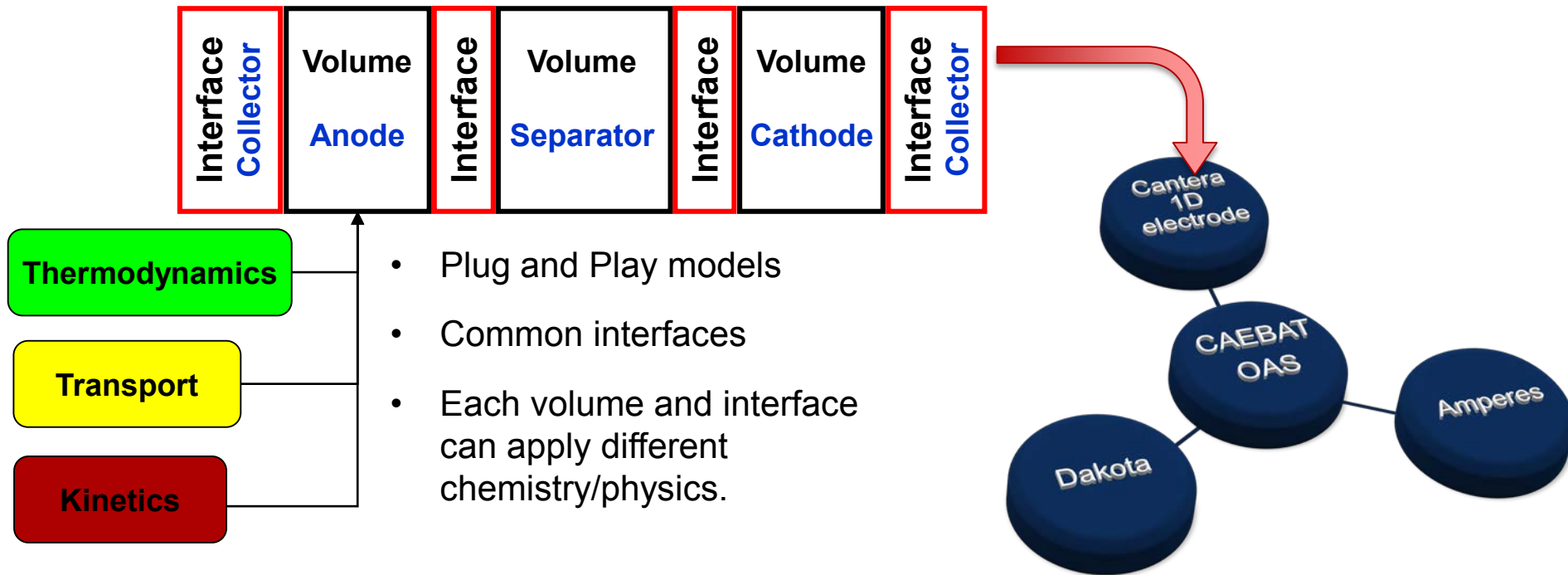
Milestones

Date	Milestone
4/1/14	Document progress on how coupling between 1DElectrode object and battery scale within CAEBAT modeling is to be carried out. Document I/O and restart strategy for integrating 1DElectrode within CAEBAT. (Complete)
10/1/14	Verification studies on electrode implementation: comparison against previously implemented models not in Electrode structure. (Complete)
10/1/14	Implement models for partially saturated porous flow within the CAEBAT/Electrode architecture. (In progress)
10/1/14	Implement plan for upscaling particle-scale calculations for bulk quantities. (Complete)
10/1/14	**Go/No-go decision**: Duplicate existing capability using the NTG and Dualfoil program using the 1DElectrode infrastructure within CAEBAT. A verification exercise will be carried out to demonstrate this basic milestone. (Complete)
4/1/15	Implement solid mechanics modeling within the CAEBAT/Electrode architecture. (In progress)
4/1/15	Document upscaling work and publish. (In progress)
4/1/15	Integrate models for SEI solubility in electrolyte. Demonstrate SEI loss or thinning as a function of the temperature. (In progress)
10/1/15	Verify solid mechanics modeling within the CAEBAT/Electrode architecture.
10/1/15	Demonstrate qualitative agreement of thermal runaway models against BATLab data.
10/1/15	Exercise battery level modeling to develop examples of thermal-runaway calculations as a function of input parameters.

Approach/Strategy

Approach

- <u>Cantera</u>: open-source C++ framework providing thermodynamics, transports, kinetics. Modular. Highly extensible.
- Recent Sandia, CSM Cantera development: non-ideal thermo, electrochemistry.
- Recent Sandia applications built on Cantera: subgrid and 1D electrode models.

Interface Collector	Volume Anode	Interface	Volume Separator	Interface	Volume Cathode	Interface Collector

Thermodynamics

Transport

Kinetics

- Plug and Play models
- Common interfaces
- Each volume and interface can apply different chemistry/physics.

Cantera 1D electrode

CAEBAT OAS

Amperes

Dakota

Oak Ridge CAEBAT open architecture for incorporating multi-physics models.

Approach/Strategy - II

Strategy:

- Incorporate Cantera applications into CAEBAT open architecture.
- Add missing capabilities (side reactions, passivation/SEI layers, gas generation, partially saturated porous flow, solid mechanics)
- Develop upscaling algorithms linking fine-scale to device-scale.
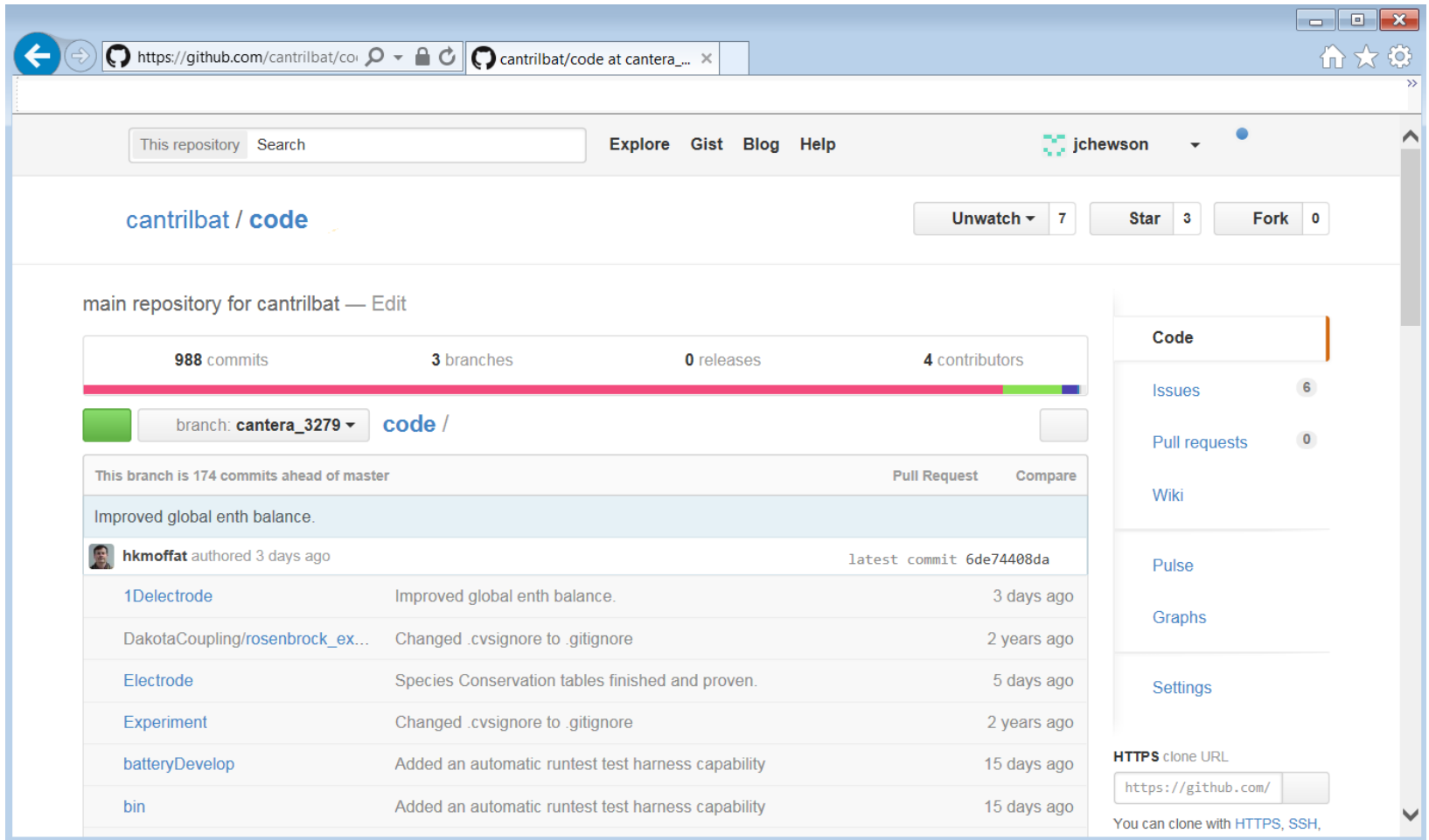- Demonstrate on thermal abuse scenario.

Milestones

- Partial saturation flow this year
- SEI layer formulations at end of year

Go/No-Go: (10/1/14) satisfied

- Duplicate existing capability (NTG and Dualfoil) with Cantera/1DElectrode within CAEBAT architecture. Developed generalized Butler-Volmer reaction formalism, OCV specification algorithm, and new transport coefficient algorithms for organic solvent-salts with Cantera.

Accomplishments - I

- <u>Cantrilbat </u>open source licensing approved. Repository on github.com/cantrilbat

Accomplishments – II
Coupling Cantrilbat 1DElectrode with CAEBAT

Electrical and thermal data from 1DElectrode are inputs to CAEBAT Amperes interface: Definitions for "Quick" Open circuit potentials and resistances

$$R_{anode} = \frac{\left(\phi^a_{solid,left} - \phi^a_{lyte,right}\right) - Ess\_a}{I}$$

$$R_{cathode} = \frac{Ess\_c - \left(\phi^c_{solid,right} - \phi^c_{lyte,left}\right)}{I}$$

$$R_{sep} = \frac{\left(\phi^a_{lyte,right} - \phi^c_{lyte,left}\right)}{I}$$

Volts, ϕ

$\phi^c_{solid,right}$

$\eta = -0.2$

$\Phi\_a = 3.80$

Ess_c=3.97

Electrolyte Potential

$\eta = 1.2E-2$

Ess_a=-4.1E-2

$\phi^a_{lyte,right}$

$\phi^c_{lyte,left}$

$\Phi\_lyte = 1.2E-2$

0.0

$\Phi\_a = 1.0E-6$

$\phi^a_{solid,left}$

ANODE   separator   CATHODE
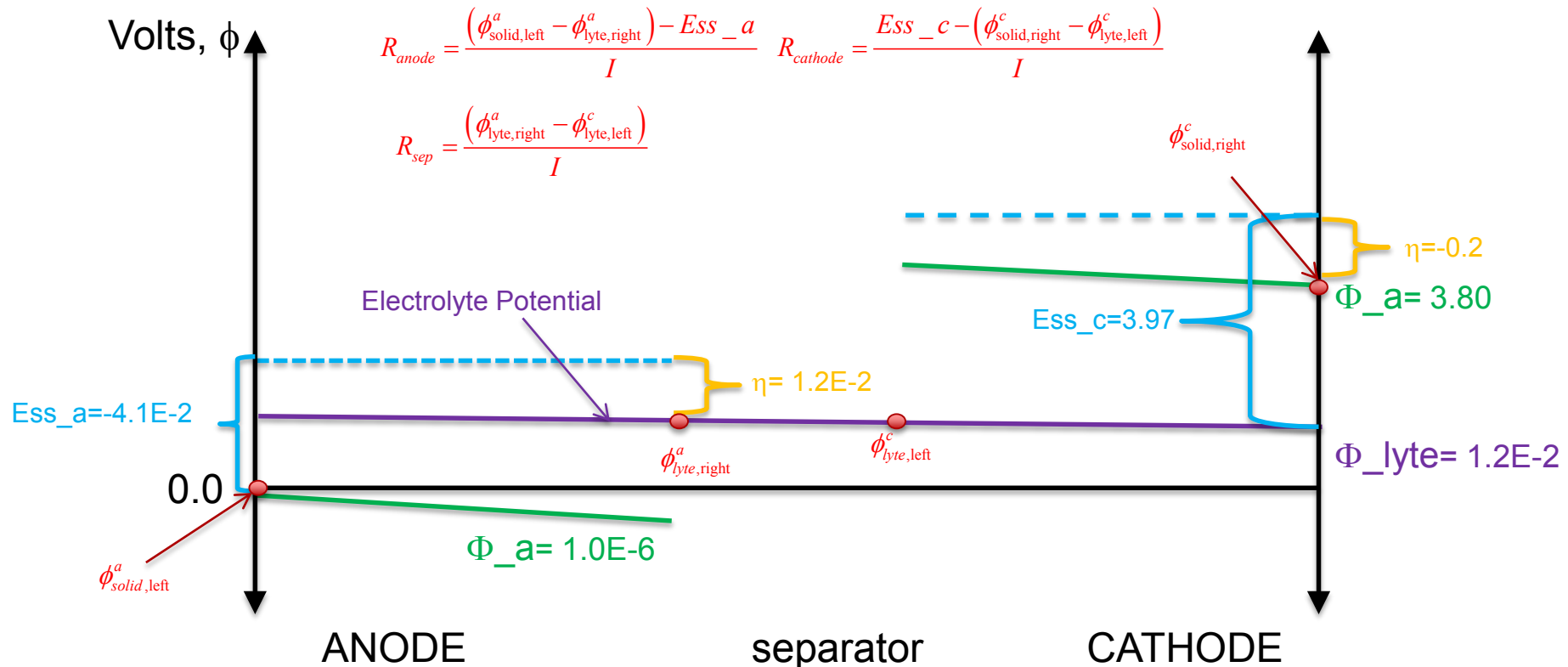
(Ess are the half-cell open circuit potentials of the end CV's)

$$R_{total} = \frac{\left((Ess\_c - Ess\_a) - \left(\phi^c_{solid,right} - \phi^a_{solid,left}\right)\right)}{I}$$

Sandia National Laboratories

Test Case : Unrolled Cell (Electrochemical-Thermal)

- Coarse mesh to model thermal transport over entire domain
- Divide domain into multiple zones
- On each zone run Cantrilbat concurrently at discharge current of 0.3 A/cm^2
- Average zonal quantities of interest transferred through state file.
- Cantrilbat keeps its own more detailed restart file.

Electrochemistry (Cantrilbat)

T_{avg} q_{avg}

Battery State File

q_{avg} T_{avg}

Thermal (Amperes)

328.6
321.0
313.4
305.8
298.1
Max: 328.6
Min: 298.1
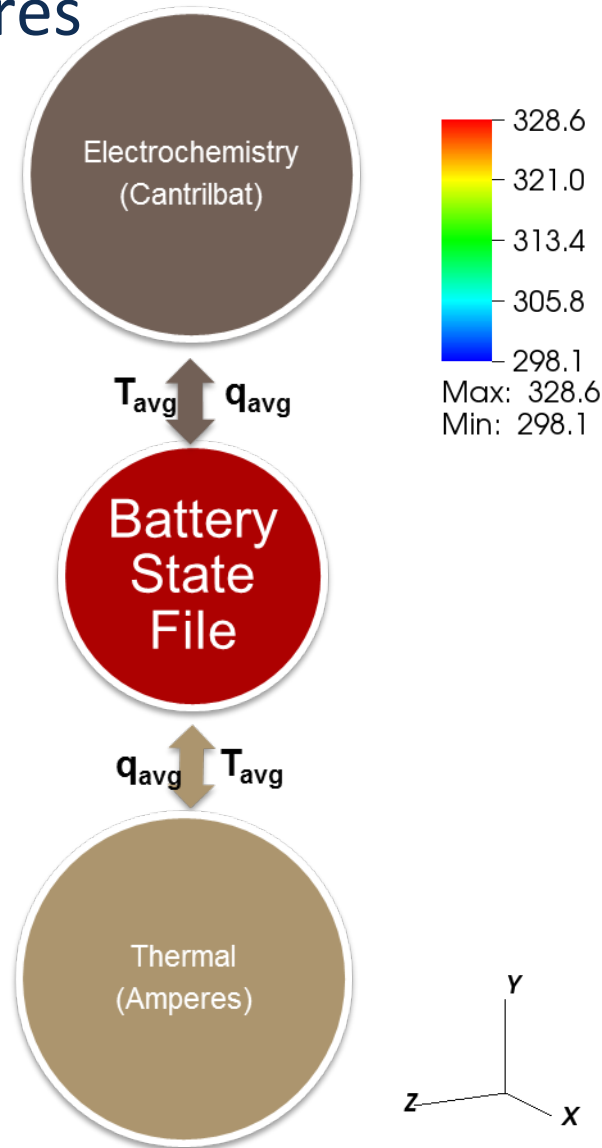
(Not to scale)

Total Enthalpy Formulation implemented for batteries

$$\sum_{\alpha}\left[\frac{d\left(\Theta_{\alpha}c_{\alpha}\tilde{H}_{\alpha}\right)}{dt}+\nabla\Box\left(c\tilde{H}\boldsymbol{v}_{Darcy}\right)\right]=\nabla\bullet\left(\lambda_{composite}\nabla T\right)-\sum_{\alpha}\sum_{k}\nabla\Box\left(\hbar_{k}J_{k}\right)+\Phi_{Darcy}$$

- where $\hbar_{k}=h_{k}+z_{k}F\Phi_{\alpha}$ is the electrochemical enthalpy

- BV Heat source term easily expressed in terms of electrochemical enthalpy:

$$q=\sum_{j}a\,i_{j}\left(V-E_{j}\right)+\sum_{j}a\,i_{j}T\frac{dE_{j}}{dT}=-\sum_{j}\sum_{k}a\,\alpha_{jk}\hbar_{k}\dot{S}_{j}$$

- Implementation is a first for battery and electrochemistry community provides a natural approach for handling multiple phases and multi-physics terms such as solid mechanics and partial saturation.
- Approach leads to a conservative implementation, where global energy balance can be checked.

Accomplishments: Example calculation for total enthalpy equation
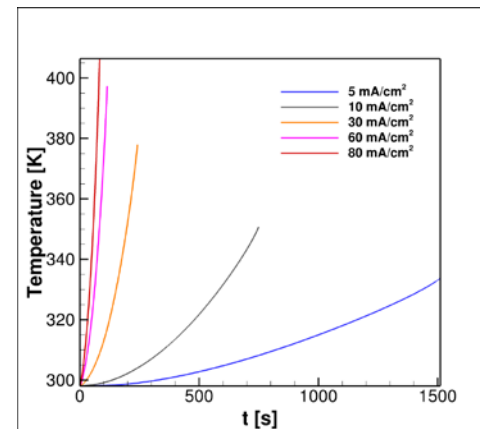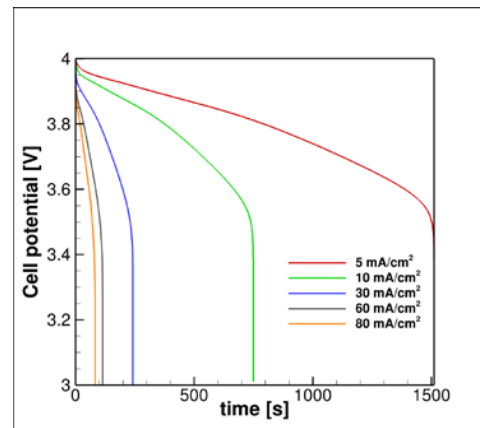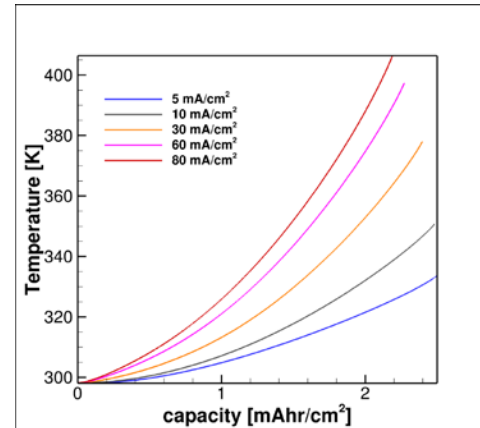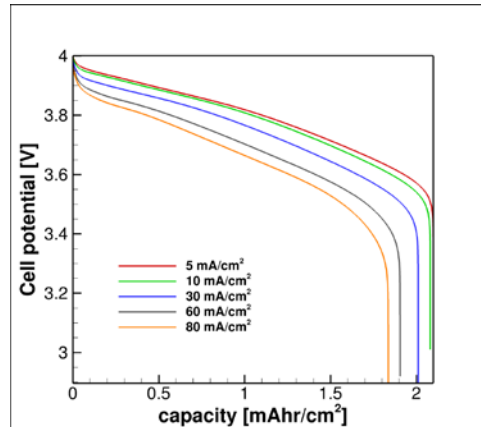

Parameters for MCMB anode and LiCoO2 cathode with LiPF6 EC-DMC electrolyte modeled after (Mao et al. JPS, 271 (2014) 444)

Demonstrated core electrochemistry capabilities

Cantrilbat 1Delectrode evaluated on dualfoil test cases.

- Comparison not perfect because of dualfoil unknowns for some parameters
- Required fitting OCV and generalized B-V with affinity formulation
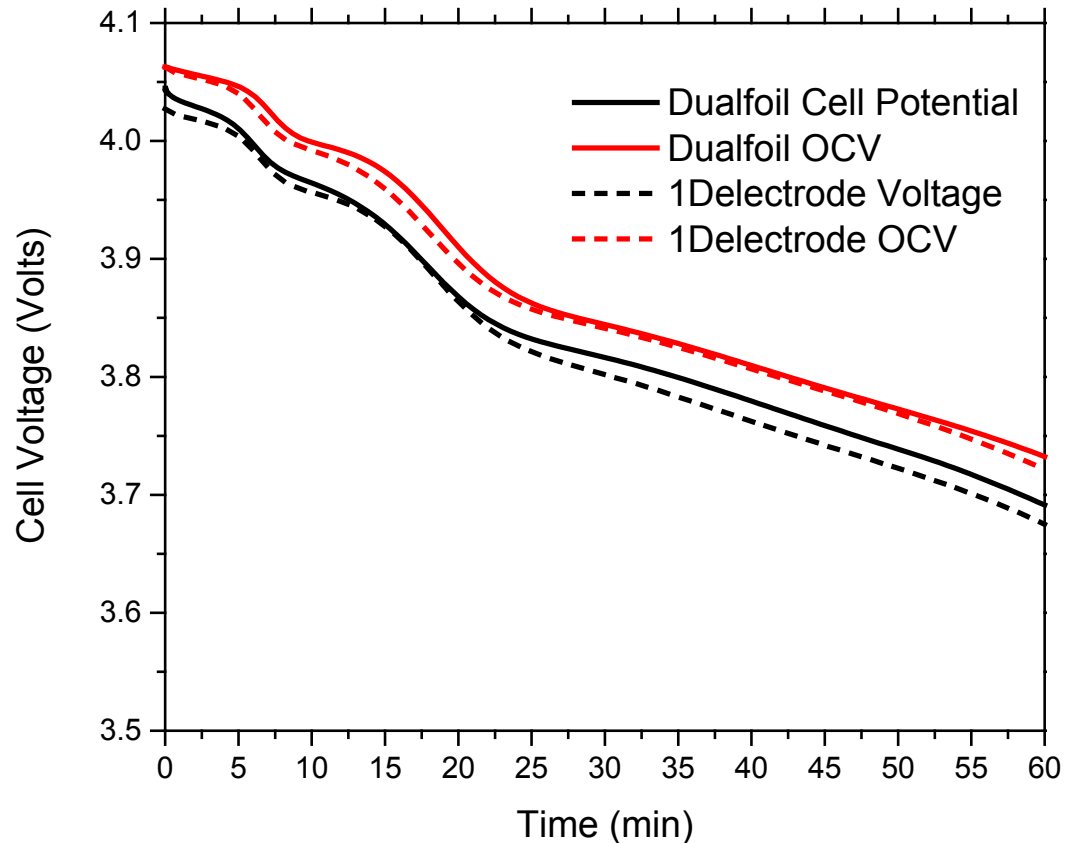
Affinity formulation developed based on transition state theory and existence of surface phases that affect interphase chemistry.

$$ROP_i = k_{f,i}^c s_m \prod_{k=0}^{N} a_k^{\lambda_{ik}} \exp\left[\frac{-\beta_i^f\left(\sum_k \nu_{k,i} z_k \Phi_k\right)}{RT}\right]\left(1 - \exp\left[\frac{-A^\zeta}{\sigma_i RT}\right]\right)^{n_i} = i_o\left(\exp\left(\frac{\beta^f F n_s \eta_s}{RT}\right) - \exp\left(\frac{-\left(1-\beta^f\right) F n_s \eta_s}{RT}\right)\right)$$

Partially saturated flow and cell pressurization implementation developed

- Implementation documentation for implementation of partially saturated flow with Darcy velocities have been developed based on Sandia work on CO_2 sequestration.

$$\frac{\partial\left(\phi S_\beta C_{\beta,k}\right)}{\partial t} + \nabla \bullet \left[C_{\beta k}\left(\mathbf{v}_\beta + \mathbf{V}^d_{\beta k}\right)\right] = \dot{r}_{\beta k} + Q_{\beta k}, \qquad \beta = l \text{ or } g \qquad \boldsymbol{v}_\beta = -\frac{\boldsymbol{k}\underline{\underline{k}}_{r\beta}}{\mu_\beta}\left(\nabla p_\beta - \rho_\beta \mathbf{g}\right)$$

- Pressurization capability has been roughed out and will be completed shortly.

$$\frac{d(C_{c,g}V_c X_k^{cavity})}{dt} = s_{g,k}^{cavity} + \sum_j V_j\, a_j^{cavity}\left(\left\langle X_{k,j} \middle| X_k^{cavity}\right\rangle C_G v_G^{Cacvity} + J_{k,j}^{Cavity}\right) + \sum_j V_j\, a_j^{cavity} Q_{j,k}^l$$

- Capillary pressure and volume of liquid is adjusted as the cell is pressurized

$$p_{l,j} = P_{G,B} - p_c^o + \eta\left(h_j - h^o\right)$$

- With these capabilities gas phase generation processes due to cook-off processors or gas generation from electrolyte electrochemical reactions may be implemented.

Solid mechanics capability implementation developed

- While only 1D, solid mechanics capability resolves issues of stress state of particle pack that has been shown to have significant effects on internal resistances and capacity fade. Elastic, isotropic treatment, with shear components untracked. Effective stress treatment

$$\nabla \square \sigma = \nabla \square \left(\sigma^{eff} \right) - \nabla \square \left(bp\mathbf{I} \right) = \nabla \square \left(2G \left(\mathbf{\varepsilon}'_{ij} - \frac{1}{3} \mathbf{\varepsilon}'_{kk} \, \delta_{ij} \right) + \frac{K}{3} \mathbf{\varepsilon}'_{kk} \, \delta_{ij} \right) - \nabla \square \left(bp\mathbf{I} \right) = 0$$

$$\mathbf{\varepsilon}' = \left(\mathbf{\varepsilon}_{total} - \mathbf{\varepsilon}_{SF} \mathbf{I} - \alpha \left(T - T_o \right) \mathbf{I} + \beta (P - P_o) \mathbf{I} \right)$$

- ε_{sf} is the stress free strain state within the battery
- Resolves trade-off between porosity changes and electrode global movement using a one parameter fitting parameter.

$$\varepsilon_{SF} = \chi \varepsilon_{SF}^{particle} \qquad\qquad V_{particle} = V_{particle}^{o} \left(1 + \varepsilon_{SF}^{particle} \right)^3$$
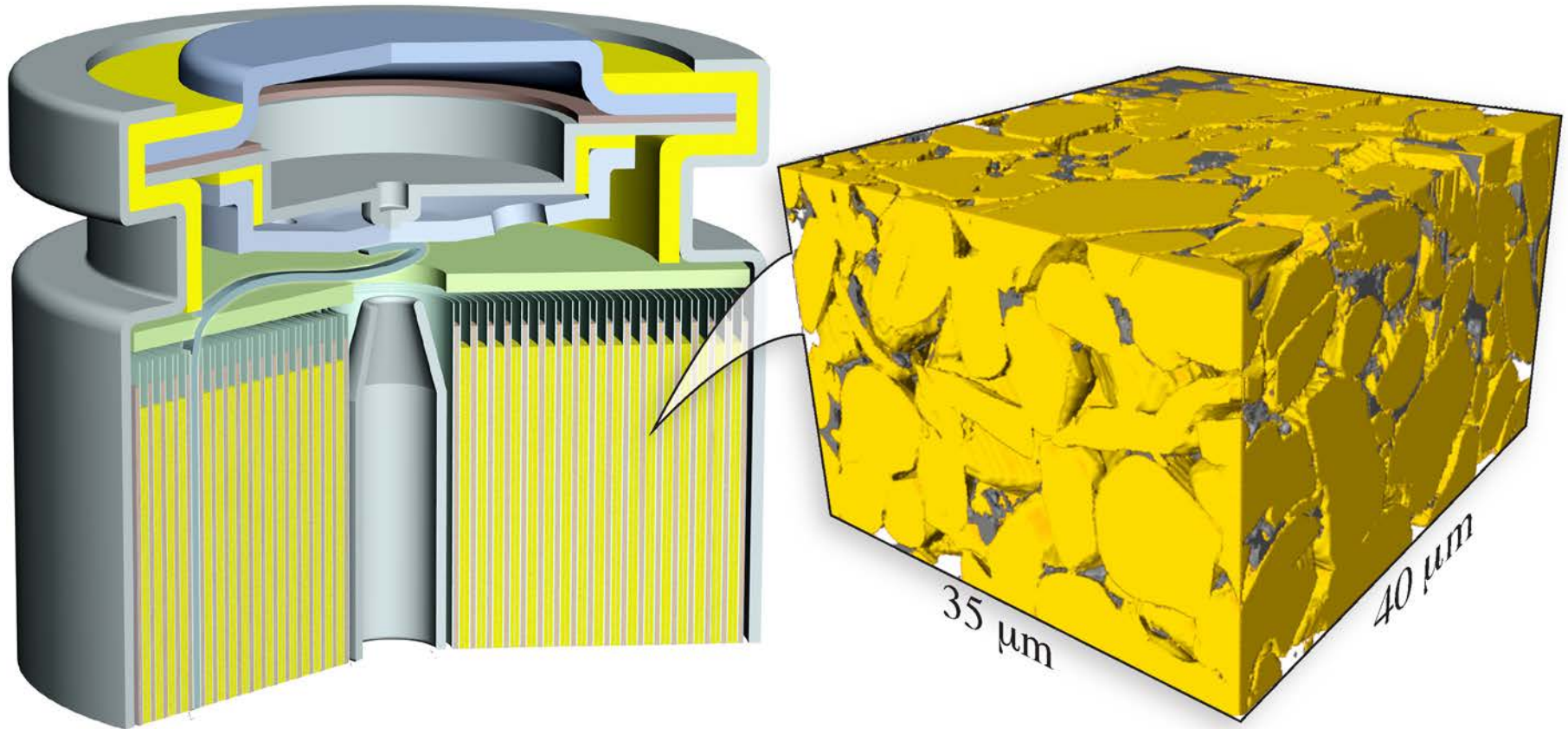
- A balance on the solid volumes within the battery couples the solid mechanics to the porosity,

$$\frac{d(1-\phi)}{dt} + \nabla \square \left[(1-\phi) \mathbf{u}_s \right] = \sum_{solids} \frac{d\phi_\alpha}{dt}$$

Models of realistic electrode microstructures provide information that is unavailable from spherical models

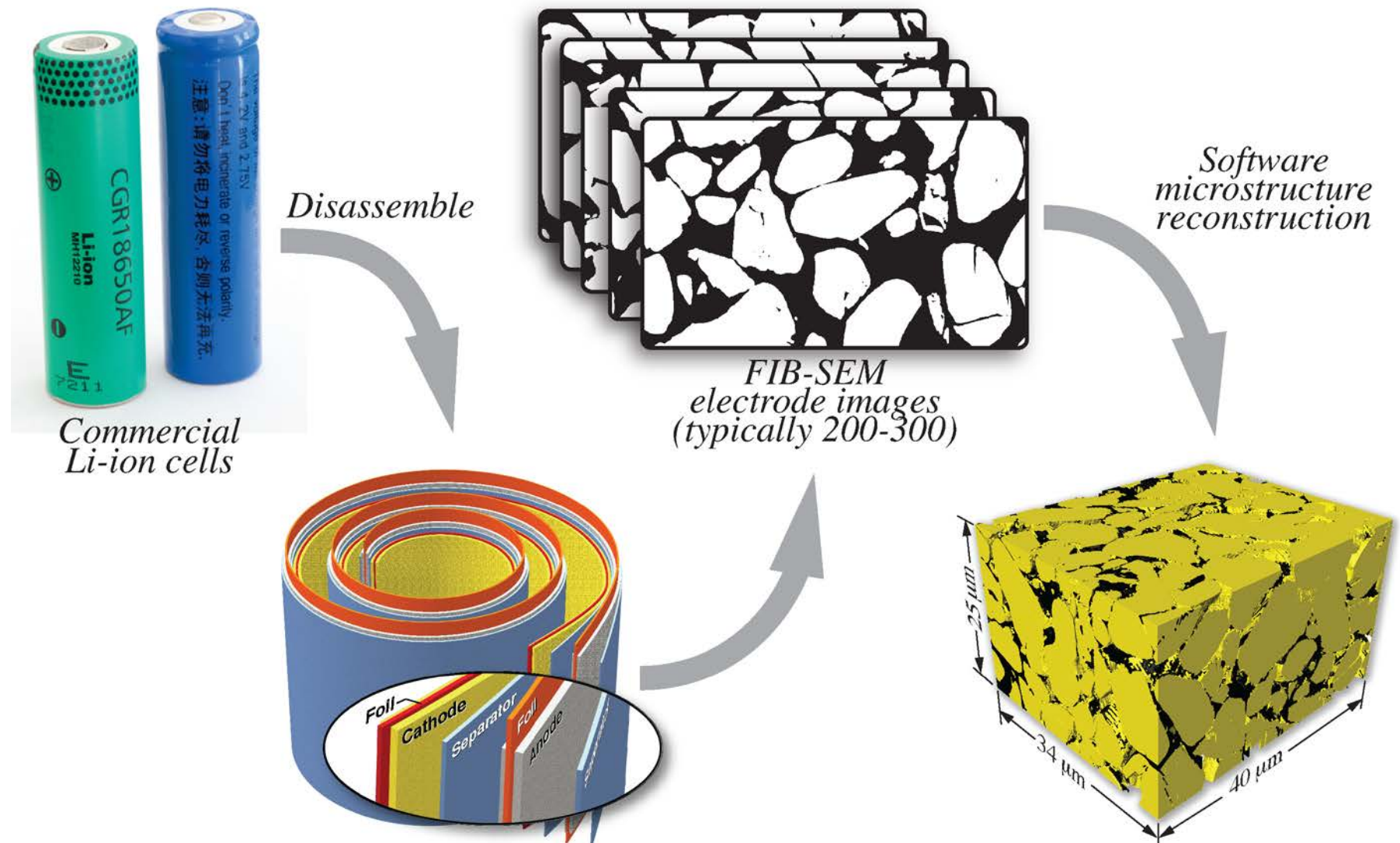Actual electrode microstructure is geometrically complex
  • Predicting microscale electrochemistry is computationally challenging
  • Upscaling is needed understand practical cell performance
  • Even at the cell scale, the geometry and materials mix is complex

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Actual electrode microstructures can be reconstructed via tomographic interrogation

Commercial Li-ion cells

Disassemble

FIB-SEM electrode images (typically 200-300)

Software microstructure reconstruction

Foil — Cathode — Separator — Foil — Anode

25 μm
34 μm
40 μm

• Wiedemann, Goldin, Barnett, Zhu, Kee, *Electrochimica Acta,* 88:580-588 (2013)

Reconstructed electrode structures are discretized as the basis for detailed computational analysis

23 µm

48 µm

46 µm
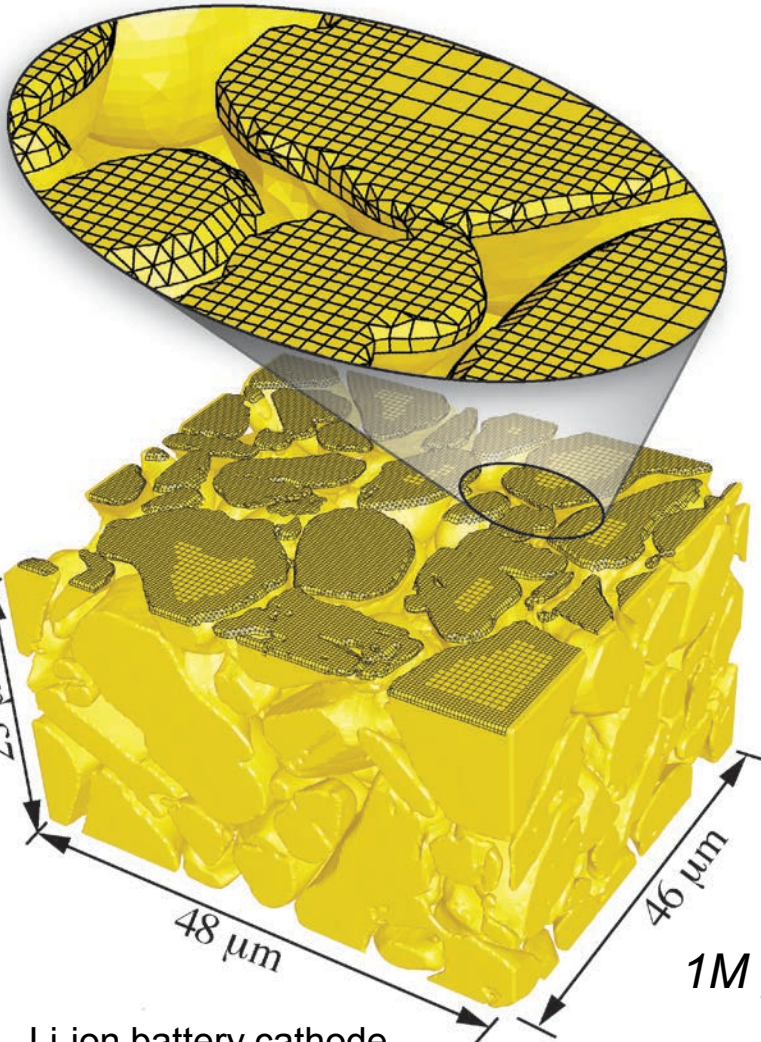
Li-ion battery cathode

Actual 3D geometry is discretized
- Solid phase and pore phase
- We have developed robust algorithms

Model transport and chemistry
- Multicomponent transport in pores
- Heterogeneous catalysis on surfaces
- Electrochemical charge transfer
- Thermal behavior at the microscale

Important questions can be answered
- How does microstructure performance?
- What are the effective properties?
- How does pore space affect ion transport?
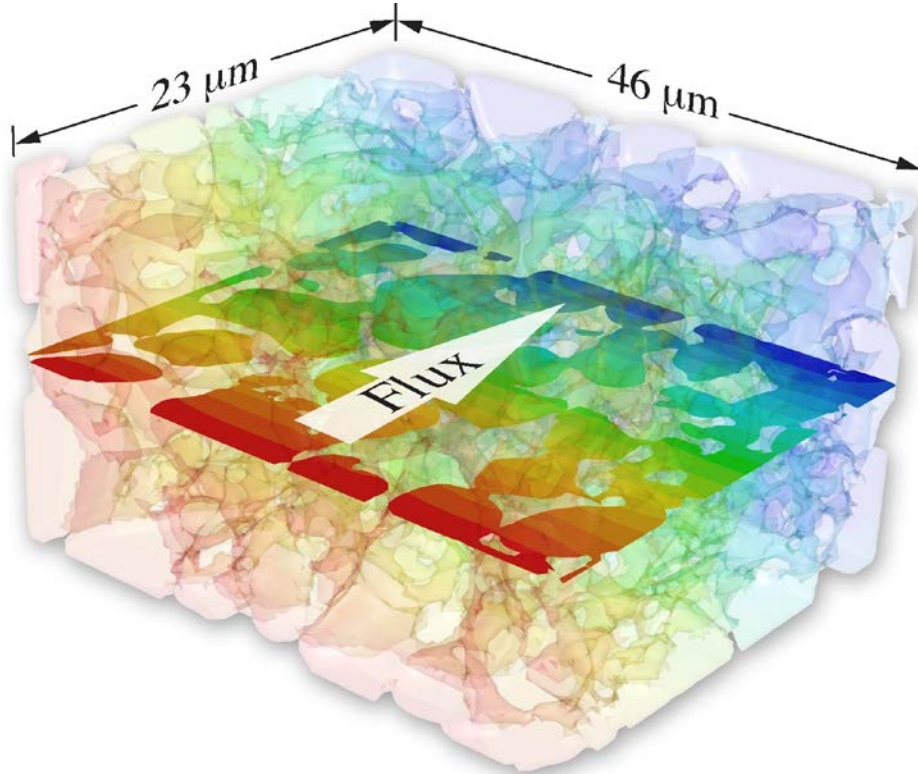- How does microstructure influence heating?

1M polyhedra cells, 4.3M faces, 2.9M nodes

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- Wiedemann, et al., *Electrochimica Acta,* 88:580-588 (2013)

Effective properties can be homogenized from microscale electrode simulations

Simulated transport through a reconstructed composite cathode

Physical properties
- Density and heat capacity
- Volume-weighted average

Conductivity
- Solve heat-conduction problem
- Evaluate heat fluxes
- Derive effective conductivity

Volumetric heat release rate
- Specify temperature
- Specify discharge rate
- Solve electrochemistry problem
- Evaluate local heat release
- Average over microscale sample
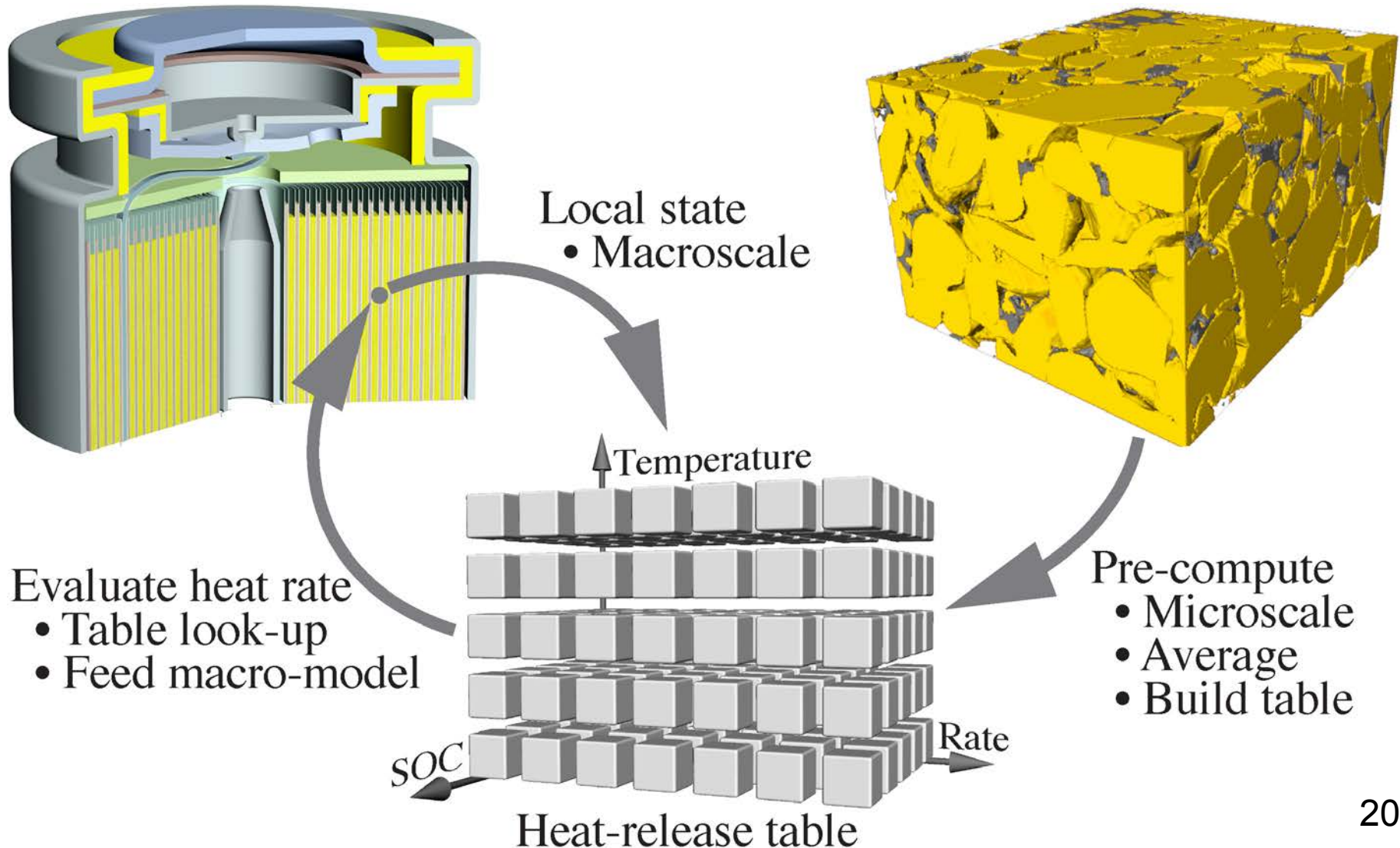
The reconstructed electrode samples are small, but representative
- *Millions of finite-volume cells*

Pre-computed table look-up may provide a viable route for up-scaling the electrochemical heating

Local state
- Macroscale

Temperature

Evaluate heat rate
- Table look-up
- Feed macro-model

Pre-compute
- Microscale
- Average
- Build table

SOC

Rate

Heat-release table

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Effective thermal properties can be derived from analysis of the resolved electrode microstructure

Volume average at microscale

$$\rho_{\text{eff}} = \frac{\rho_c V_c + \rho_e V_e}{V_c + V_e}$$

$$c_{p,\text{eff}} = \frac{c_{p,c} V_c + c_{p,e} V_e}{V_c + V_e}$$

Intrinsic cathode properties
- $\rho_c = 2328$ kg m^{-3}
- $c_p = 1269$ J kg^{-1} K^{-1}
- $k_c = 1.58$ W m^{-1} K^{-1}

Model conduction in composite

$$k_{\text{eff}} = \frac{q''}{L \Delta T}$$

- Computed flux
- Imposed temp. diff.
- Sample thickness
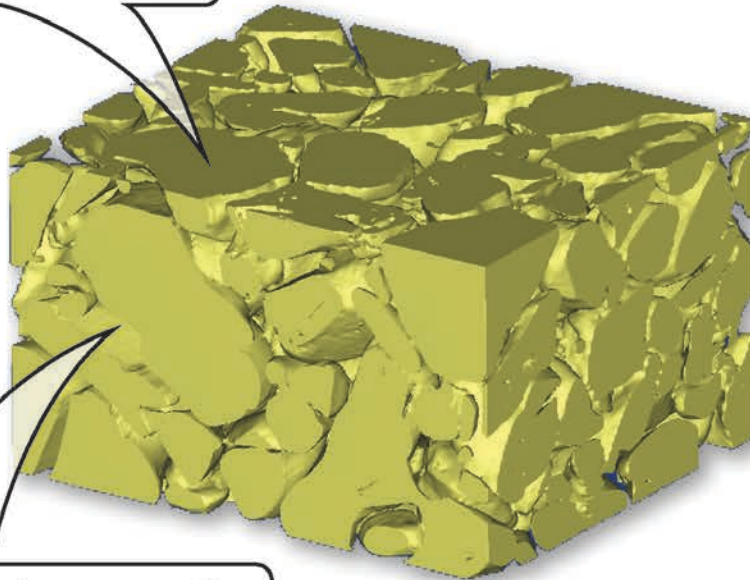
Intrinsic electrolyte properties
- $\rho_e = 1130$ kg m^{-3}
- $c_p = 2055$ J kg^{-1} K^{-1}
- $k_e = 0.60$ W m^{-1} K^{-1}

Effective cathode properties
- $\rho_{\text{eff}} = 2006$ kg m^{-3}
- $c_{p,\text{eff}} = 1481$ J kg^{-1} K^{-1}
- $k_{\text{eff}} = 1.19$ W m^{-1} K^{-1}

Collaboration and Coordination

- Team:
    - Sandia (prime) – electrochemistry, electrode models, additional physics integration involving thermal runaway
    - Oak Ridge – CAEBAT open architecture, integration.
    - Colorado School of Mines – upscaling (average values and statistical variations)

- Collaboration/project leverage
    - Sandia internal programs on defense-related battery programs.
    - Duracell Crada -> Modeling alkaline batteries in 1,2, and 3D with same software

- Soliciting other groups – facilitated by open source github site:
    - Prof. Tito Busani UNM (EE dept)   Li-S battery modeling
    - Reese Jones, Marie Kane, SNL, Li-Air simulations

Remaining Challenges –
Get infrastructure ready for:
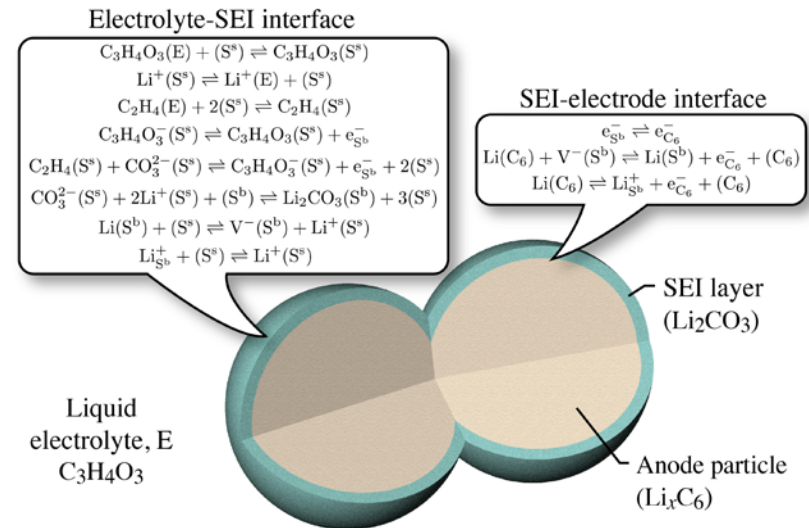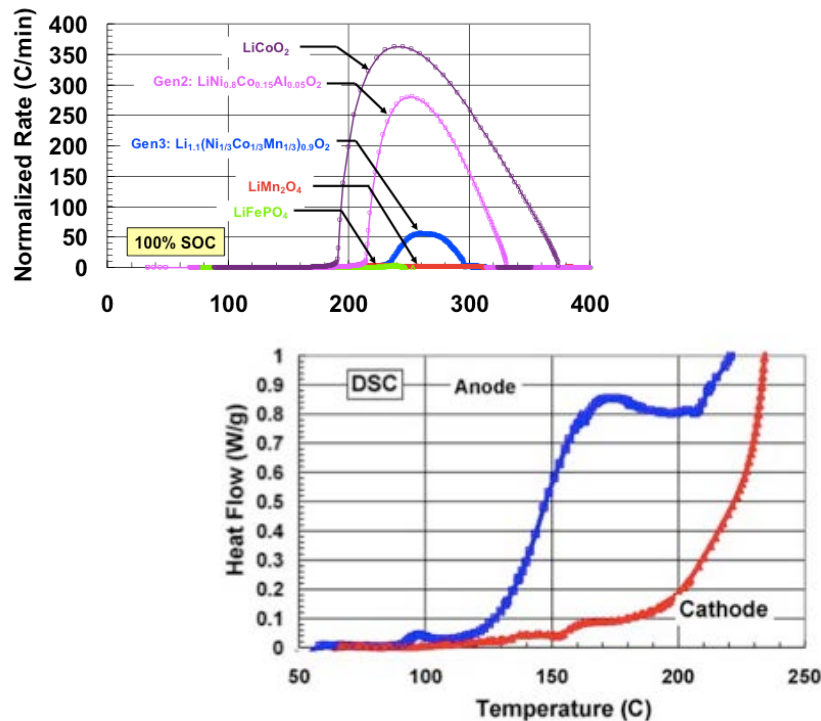
- We seek to develop a software platform to model thermal abuse using a speciation and fully reversible-thermodynamics approach.

Proposed future work

FY15 end

- Finish Implement solid mechanics, partial saturation models, and pressurization models to enable multi-phase capability

- Document upscaling algorithms.

- Integrate SEI models. Demonstrate capabilities. Compare with BATLab data.

  Last item is a key project goal: demonstration of flexibility to adopt literature models to address complicated, multi-physics issues within CAEBAT architecture.

LongTerm

- Develop partnerships through open source platforms to create synergistic programs to combine experimental measurements, upscaling of molecular modeling, and software at the cell level to address the development of battery mechanisms.

Response to Reviewer Comments

- No comments received.

Summary

- We are on schedule to complete the major goals.

- New open-source Multiphysics battery simulator has been stood up (cantrilbat.github.com) that can be used for mechanism development.

- We have integrated the model into the CAEBAT architecture with validation underway. A list of tasks has been generated to complete the validation.

- We have carried out calculations at the pore scale developing an understanding of Joule heating and local stress concentrations, and have developed plans based on heat release look-up tables.

Technical Back-Up Slides

Cantrilbat Electrode Objects

Electrode_CSTR - production
    CSTR approximation with surface interfacial Rxn object. Model for intercatated electrode without solid phase diffusion limitation

Electrode_MP_RxnExtent - production
    Single Extent Variable with an effective SS diffusion model. Multiple OCV Regions allowed

Electrode_InfCapacity - production
    surface interfacial Rxn object with non-varying solid phase

Electrode_MultiPlateau   - production
    Phase Change Electrode model. Multiple OCV Regions allowed
    Effective Diffusion in prep (EAR99, thermal battery)

Electrode_SimplePhaseChangeDiffusion - frozen – to be hardened.
    Phase Change Electrode model with diffusional capacitance terms.

Electrode_SimpleDiffusion , Electrode_DiffTALE   - DONE
    Model for intercalated electrode with solid phase diffusion. TALE method handles volumetric expansion and lattice source terms.

Electrode_RadialDiffRegions   - initial planning
    Expansion of SimpleDiffusion to multiple regions separated by internal interfacial rxns. (SEI) layer

Cantera's electrochemistry treatment

Object oriented treatment of homogeneous and heterogeneous phase

Speciation is treated via a full specification of the chemical potentials of all species including the electron.

Full treatment of Pitzer's brine thermodynamics, molten salt non-ideal thermodynamics, mixtures of organic solvents, etc. Usually, one ionic-species in the mixture must be specified via a convention. Treatment of organic solvents in the works for this project

Electrochemical reactions at interfaces are treated as reversible reactions with potentials modified by the electrochemical potentials of the species – single reaction is compatible with Butler-Volmer formulation, adsorbate-modified behavior can model realistic experiments.

Accomplishments: Electrode Evolution Model

- Finite-capacity porous electrode model:
  - Electrode depletion tracked with representative particle sizes, densities.
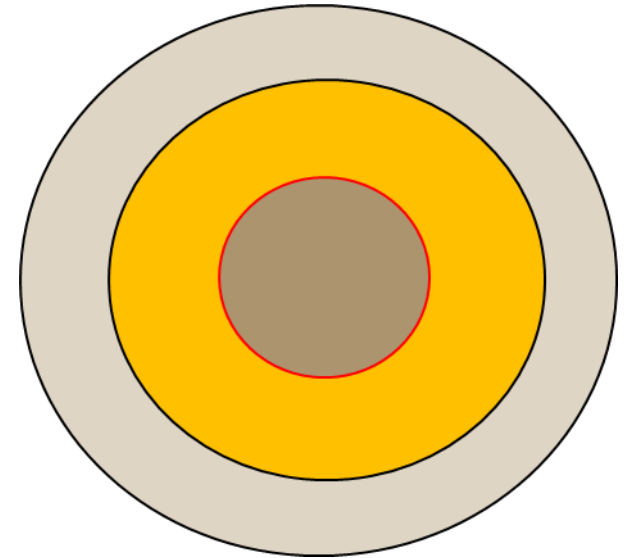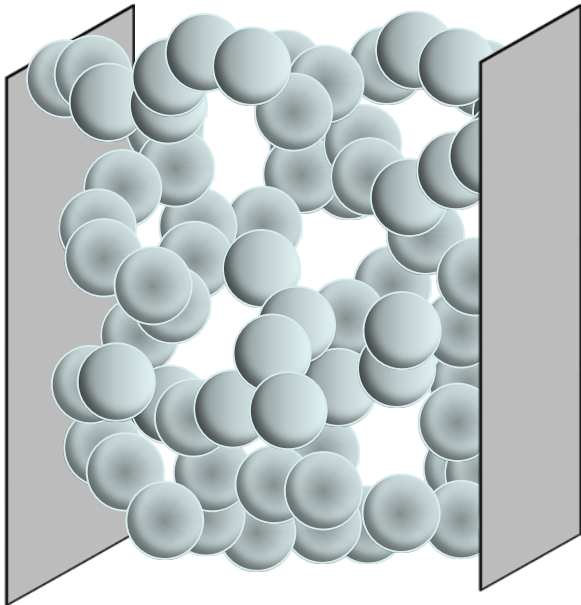
- Multiple plateaus can simultaneously react in our implementation of the shrinking core model.

- Reactions at phase interfaces.

- Diffusional losses associated with transport from inner cores.

- Added Radial diffusion electrode objects (TALE method)

Accomplishments – Understanding numerical issues associated source terms with state variables

Electrode Source term is turned into a time dependent integral over the time step of the outer loop.

Enables modular software architecture – Already in 3D Code, Aria!

Example – continuity equation for electrolyte species includes a source term from the electrode reaction,

$$\frac{\left(V_i\, C_T \phi X_k \right)_{n+1} - \left(V_i\, C_T \phi X_k \right)_n}{t_{n+1} - t_n}$$

$$+ n_{iL} \bullet \left[A_{iL} C_T X_k \left(\mathbf{v} + \mathbf{V}_k \right) \right] + n_{iR} \bullet \left[A_{iR} C_T X_k \left(\mathbf{v} + \mathbf{V}_k \right) \right] = \left(V_i\, w_k \right)_{n+1}$$

Source term is formally replaced by an integral over the time step:

$$w_{k,n+1}\left(A_{n+1}, \alpha, t \right) \quad \rightarrow \quad \frac{\displaystyle\int_{t_n}^{t_{n+1}} w_k\left(A_{n+1}, \alpha, t \right) dt}{t_{n+1} - t_n}$$
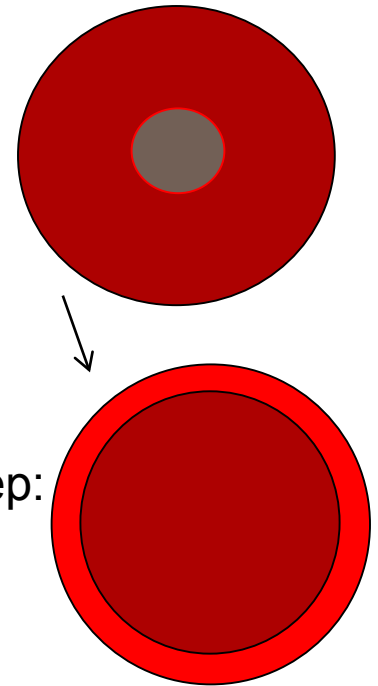
Key to isolating and uncoupling the complexity between 1D and subgrid models: Requirements: Predictor-corrector time step strategy:

Implicit stiffness coupling still requires jacobian

Essential first task: Incorporate Electrode object into CAEBAT

At the end of the first year we expect to be able to duplicate Dualfoil capability using the 1DElectrode infrastructure within CAEBAT.
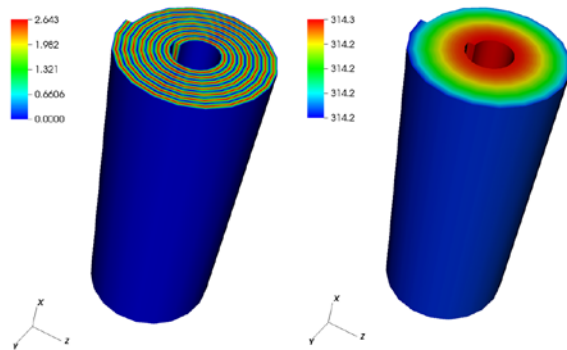
Integration issues initially addressed

A verification exercise is being carried out to demonstrate this basic milestone.

Lessons learned, items to be accomplished from dualfoil comparison:

- Include direct parameterization of OCV as an important option in 1DElectrode and Electrode modeling. Note, this is limiting though as it prevents relating molecular structure to OCV through thermo modeling.
- Add empirical but often used exchange current density formulation. Not mass-action based from Marcus theory, but widely used to correlate data
- Either include parameterization for temperature dependence of all thermo parameters and fit to thermo of OCV, or model the temperature dependence of OCV directly.

Internal shorts produce locally high heat release, significantly altering the thermal response

Initiate internal short

1C, 200 s

250 s

300 s

350 s

400 s

298 K   310 K

33
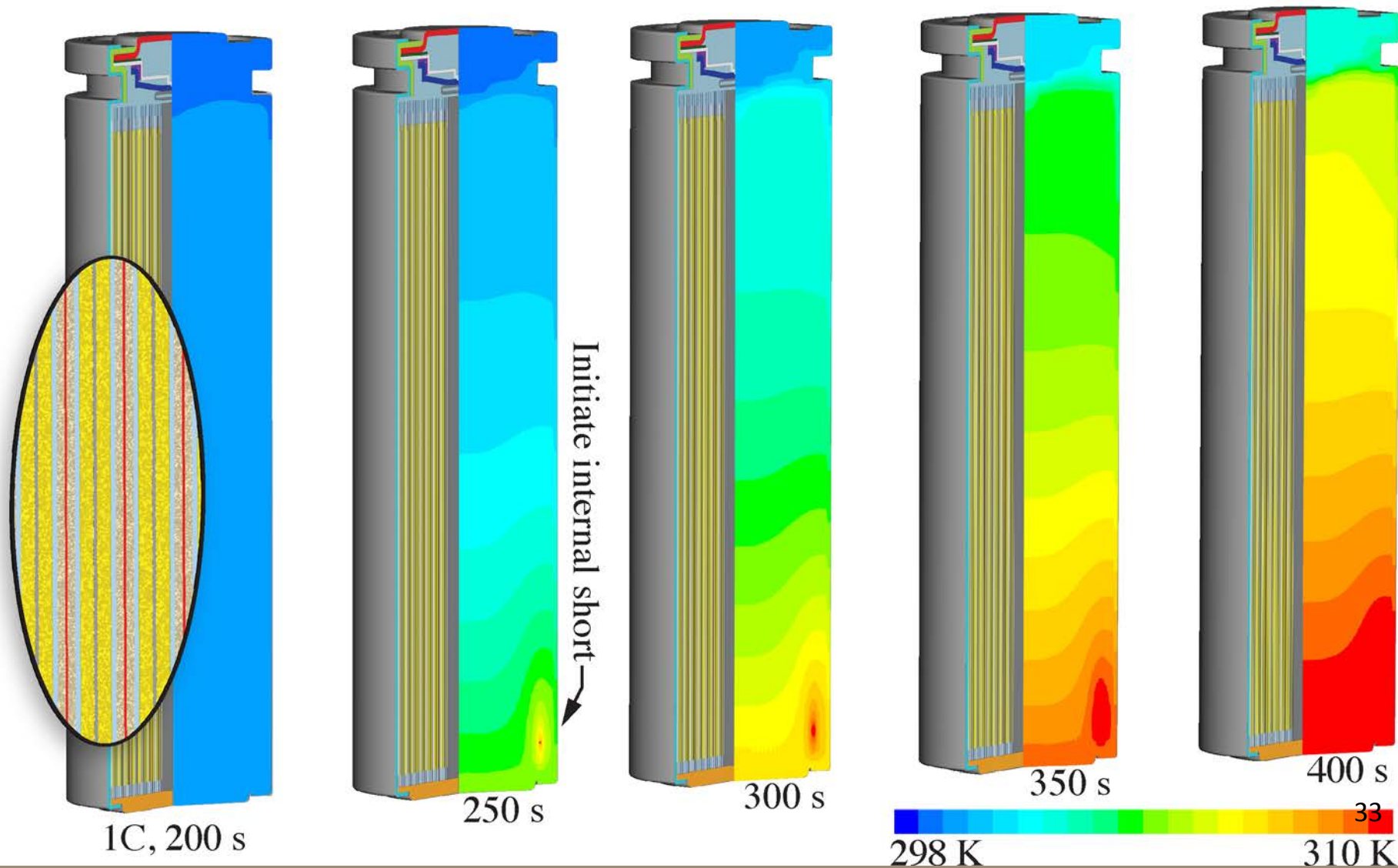
Temperature variations at the microscale are small, even with very high heat generation rates

120 C external short
(after 1 s)
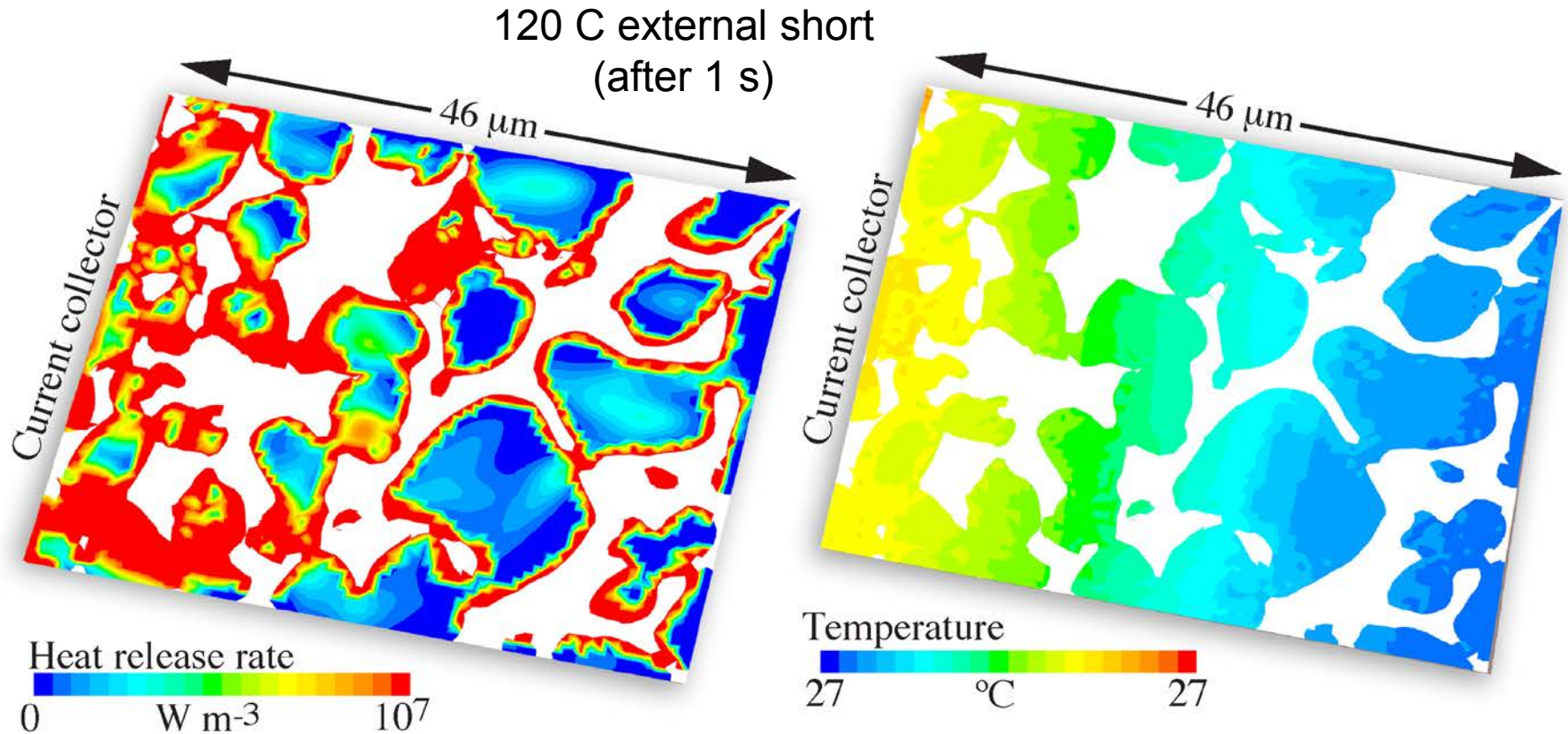
Relatively high conductivity effectively spreads heat over small distances

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The cathode charge-transfer chemistry is based on a semi-empirical Butler-Volmer formulation

Butler-Volmer charge transfer

$$\dot{s}_{\mathrm{e}} = i_{\mathrm{o}} \left[\exp\left(\frac{\alpha_{\mathrm{a}} F \eta_{\mathrm{act}}}{RT} \right) - \exp\left(-\frac{\alpha_{\mathrm{c}} F \eta_{\mathrm{act}}}{RT} \right) \right]$$

Activation overpotential

$$\eta_{\mathrm{act}} = \Phi_{\mathrm{ed}} - \Phi_{\mathrm{el}} - E^{\mathrm{eq}}$$

Equilibrium electric potential difference

$$E^{\mathrm{eq}} = E_{\mathrm{ref}}^{\mathrm{eq}} + \frac{\partial E^{\mathrm{eq}}}{\partial T} (T - T_{\mathrm{ref}})$$

Exchange current density

$$i_{\mathrm{o}} = k_{\mathrm{r}} F C_{\mathrm{Li+}}^{\alpha_{\mathrm{a}}} \left[C_{\mathrm{Li}}^{\mathrm{max}} - C_{\mathrm{Li}} \right]^{\alpha_{\mathrm{a}}} C_{\mathrm{Li}}^{\alpha_{\mathrm{c}}}$$

Guo and White, *J. Electrochem. Soc.*, 158:A1166-A1176 (2011)

Cathode equilibrium reference potential

$$E_{\mathrm{p,ref}}^{\mathrm{eq}} = 4.04596 + \exp\left(-42.30027\theta_{\mathrm{p}} + 16.56714\right) - 0.04880 \arctan\left(50.01833\theta_{\mathrm{p}} - 26.48897\right)$$
$$-0.05447 \arctan\left(18.99678\theta_{\mathrm{p}} - 12.32362\right) - \exp\left(78.24095\theta_{\mathrm{p}} - 78.68074\right)$$